WSC – CAM – IV A

Quality Assurance and Quality Control Requirements **for the Method For The Determination of Volatile Petroleum Hydrocarbons (VPH), MADEP-VPH-98-1** for the Massachusetts Contingency Plan (MCP)

Document Status: Interim Final

Please provide comments to the Department on this Interim Final Document on or before 16 August 2002.

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Document Chronology

Revision	Status	Date
0	Public Comment Draft	5 October 01
1	Interim Final	12 July 02

IV. Petroleum Hydrocarbon Methods

A. Quality Assurance/Quality Control (QA/QC) Requirements and Performance Standards for the Method For The Determination of Volatile Petroleum Hydrocarbons (VPH), MADEP-VPH-98-1

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1.0 QA/QC Requirements For The Volatile Petroleum Hydrocarbons Method

1.1 Method Overview

The Volatile Petroleum Hydrocarbons Method (the "VPH Method") uses purge-and-trap sample concentration, gas chromatographic (GC) separation and in-series Photoionization and Flame Ionization Detectors (PID/FID) to identify and quantify both target analytes and method-defined aliphatic and aromatic hydrocarbon fractional ranges in water, soils and sediments. Volatile aliphatic hydrocarbons are collectively quantified within two specific ranges: C_5 through C_8, and C_9 through C_{12}. Volatile aromatic hydrocarbons are collectively quantified within the C_9 to C_{10} range. These aliphatic and aromatic hydrocarbon ranges correspond to a boiling point range between approximately 36°C and 220°C. This method may also be used to identify and quantify benzene, toluene, ethylbenzene, xylenes (BTEX), naphthalene, and methyl-tert-butylether (MTBE) as Target Analytes.

The VPH Method is designed to complement and support the toxicological approach developed by the Massachusetts Department of Environmental Protection to evaluate human health hazards that may result from exposure to petroleum hydrocarbons (MADEP, 1994). It is intended to produce data in a format suitable for evaluation by that approach, and that may be compared to reporting and cleanup standards promulgated in the Massachusetts Contingency Plan (310 CMR 40.0000).

Petroleum products suitable for evaluation by the VPH Method include gasoline, mineral spirits, and certain petroleum naphthas. In and of itself, the VPH Method is not suitable for the evaluation of kerosene, jet fuel, heating oils, lubricating oils, and/or other petroleum products which contain higher boiling components, or distillates of aliphatic and/or aromatic hydrocarbons that are beyond the analytical range of the VPH Method.

This method is restricted to use by, or under the supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatographs (GCs), and skilled in the interpretation of gas chromatograms for individual target analytes and petroleum hydrocarbon ranges in environmental matrices. Each analyst must demonstrate the ability to produce acceptable quantitative and qualitative results both for individual target analytes and petroleum hydrocarbon ranges with this method.

1.1.1 Reporting Limits for the VPH Method

The Reporting Limit (RL) for each of the aliphatic and aromatic fractional ranges is approximately 2 - 10 mg/kg in soil, and approximately 50 - 100 µg/L in water for the VPH Method. The RL of this method for Target Analytes is compound-specific, and ranges from approximately 0.1 - 0.2 mg/kg in soil, and 1 - 10 µg/L in water. These RLs reflect the sampling procedures and the prescriptive analytical conditions imposed by the Method.

1.1.2 Requirements for the VPH Method

Each laboratory that uses the VPH Method is required to operate a formal quality assurance program. The minimum requirements of this program consist of an initial demonstration of laboratory proficiency, ongoing analysis of standards and Laboratory Method Blanks (LMBs) as a test of continued performance, and the analysis of Laboratory Fortified Blanks (LFBs), Laboratory Fortified Matrix (LFM) samples, and LFM duplicates to assess accuracy and/or precision.

Laboratories must document and have on file an Initial Demonstration of Proficiency (IDP) for each combination of sample preparation and determinative analytical method in use. An IDP must be completed and documented when a method is initially started up or whenever a method is substantially modified by the laboratory. These data must meet or exceed the performance standards as presented in Section 10.3.1 through 10.3.3 of the VPH Method and Table IV A-2 of this method. Procedural requirements for performing the Initial Demonstration of Proficiency can be found in SW-846 Method 8000B (Section 8.4) and the VPH Method (Section 10.3). The data associated with the Initial Demonstration of Proficiency should be kept on file at the laboratory and made available to potential data-users on request. The data associated with the Initial Demonstration of Proficiency for the VPH Method must include the following:

QC Element	Performance Criteria
Initial Calibration	CAM- IIA, Table IV A-2
Continuing Calibration	CAM- IIA, Table IV A-2
Laboratory Method Blanks	CAM- IIA, Table IV A-2
Laboratory Fortified Blanks	The VPH Method, Section 10.4.2.3
Sample Duplicates	The VPH Method, Section 10.4.2.4
Surrogate Recovery	CAM- IIA, Table IV A-2
System Solvent Blanks	The VPH Method, Section 10.4.2.5
Internal Standards	CAM- IIA, Table IV A-2

Note: Because of the inherent difficulty in quantifying fractional hydrocarbon ranges and the number of QC elements associated with the Initial Demonstration of Proficiency, it should be expected that one or more of the ranges and/or target analytes may not meet the performance standard for one or more QC elements. Under these circumstances, the analyst should attempt to locate and correct the problem and repeat the analysis for all nonconformances. All nonconformances, along with the laboratory-specific acceptance criteria should be noted in the Initial Demonstration of Proficiency data. This information should be kept on-file at the laboratory.

It is also recommended that laboratories calculate in-house performance criteria for LFB recoveries, sample duplicates, LMBs and surrogate standard recoveries. These quality control elements are required for each analytical batch as described in Section

10.4.2 of the VPH Method. It may also be useful to calculate such in-house criteria for LFM and LFM Duplicates when experience indicates that the recommended performance criteria are not consistently met for fractional ranges, target analytes and/or matrices. The development of in-house performance criteria and the use of control charts or similar procedures to actively monitor laboratory performance cannot be over-emphasized

For the VPH Method, laboratory-specific control limits must meet or exceed (demonstrate less variability) the performance standards for each QC element listed on Table IV A-2. It should be noted that the performance standards listed in Table IV A-2 are based on limited laboratory performance data. Laboratories are encouraged to continually strive to minimize variability and improve the accuracy and precision of their analytical results. In all cases, the LSP must compare the results of the reported laboratory-specific performance to the analytical objectives.

1.1.3 Sample Introduction Methods

As prescribed in Section 9.1 of the VPH Method, samples for analysis are introduced into the gas chromatographic system using a purge-and-trap concentrator as described in SW-846 Methods 5030 and 5035 for aqueous and solid samples, respectively. If other sample introduction methods are utilized because of analytical circumstances, the laboratory must provide a full explanation and justification in the analytical case narrative.

1.2 Summary of Method

The VPH Method is suitable for the analysis of waters, soils, and sediments. The method includes inert gas purging, of an aqueous sample or soil methanol extract, with concentration onto an adsorbent trap, and subsequent analyses by gas chromatography.

The VPH Method is based on (1) USEPA Methods 5030, 8000, 8021, and 8015, SW-846, "Test Methods for Evaluating Solid Wastes", 3rd Edition, 1986; (2) Draft "Method for Determination of Gasoline Range Organics", EPA UST Workgroup, November, 1990; and (3) "Method for Determining Gasoline Range Organics", Wisconsin Department of Natural Resources, PUBL-SW-140, 1992.

As prescribed in Section 9.1 of the VPH Method, samples for analysis are introduced into the gas chromatographic system using a purge-and-trap concentrator as described in SW-846 Methods 5030 and 5035 for aqueous and solid samples, respectively. If other sample introduction methods are utilized because of analytical circumstances, the laboratory must provide a full explanation and justification in the analytical case narrative.

The gas chromatograph is temperature programmed to facilitate separation of organic compounds. Detection is achieved by a photoionization detector (PID) and flame ionization detector (FID), connected in series. Quantitation is based on comparing the PID and FID detector response of a sample to a standard comprised of volatile aromatic and aliphatic

hydrocarbons. The PID chromatogram is used to determine the individual concentrations of Target Analytes (BTEX/MTBE/naphthalene) and collective concentration of aromatic hydrocarbons within the C_9 through C_{10} range. The FID chromatogram is used to determine the collective concentration of aliphatic hydrocarbons within the C_5 through C_8 and C_9 through C_{12} ranges. The VPH method marker compounds and retention time windows are summarized in Table IV A-1.

Table IV A-1 VPH Method Marker Compounds

Range/ Hydrocarbon Standard	Beginning Marke Compound	Ending Marker Compound
C_5-C_8 Aliphatic Hydrocarbons (FID)	0.1 minutes before n-Pentane	0.01 minutes before n-Nonane
C_9-C12 Aliphatic Hydrocarbons (FID)	0.01 minutes before n-Nonane	0.1 minutes before Naphthalene
C_9-C_{10} Aromatic Hydrocarbons (PID)	0.1 minute after o-Xylene	0.1 minutes before Naphthalene

1.2.1 Analysis of Water Samples

Water samples may be analyzed directly without sample preparation. The analysis of water samples is described in detail in Section 9.1.2 of the VPH Method. In general, a sample aliquot is introduced to the purge chamber using a 5 mL gas-tight syringe. If necessary, samples may be diluted prior to injection into the purge chamber. In such cases, sample dilutions must be performed as expeditiously as possible and the diluted sample should be transferred to a gas-tight syringe without delay.

1.2.2 Analysis of Soil and Sediment Samples

Soil and sediment samples are dispersed in methanol to extract the volatile organic constituents. A portion of the methanol extract is then extracted/concentrated by purge-and-trap and analyzed by GC. Methanol may be added in the field or in the laboratory if the samples are collected in specially designed air-tight samplers. The desired ratio of methanol-to-soil is 1 mL methanol/1 gram soil, +/- 25%. In either case, an aliquot of the extract is added to reagent water to produce a 5 mL adjusted sample volume and introduced into the gas chromatograph using a purge and trap concentrator. The volume of the aliquot will depend on the anticipated VPH concentration. ***Be advised that the volume of methanol aliquot added should not exceed 200 µL, to preclude adverse solvent front and trap breakthrough difficulties***

1.3 VPH Method Interferences

Impurities in the purge gas, and from organic compounds out-gassing from the plumbing ahead of the trap, account for the majority of system contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks. The use of non-polytetrafluoroethylene (non-PTFE) plastic coating, non-PTFE thread sealants, or flow controllers with rubber components in the purging device must be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. These compounds will result in interferences and/or false positives.

1.3.1 Sample Contamination

Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample vial during shipment and storage. A trip blank prepared from organic-free reagent water (for aqueous samples) or methanol (for soil and sediment samples), and carried through sampling and handling protocols, serves as a check on such contamination.

1.3.2 Cross- Contamination

Contamination by carryover can occur after high-concentration samples are analyzed. Whenever an unusually concentrated sample is analyzed, it should be followed by an analysis of organic-free reagent water to check for cross-contamination. The trap and other parts of the system
are subject to contamination. Therefore, frequent bake-out and purging of the entire system may be required.

1.3.3 General Precautions

As a general precaution, the laboratory where volatiles analysis is performed should be completely free of solvents. The analytical and sample storage areas should be isolated from all sources of potentially interfering volatile organics. All GC carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory workers' clothing previously exposed to potentially interfering volatile organics during common laboratory activities can contribute to sample contamination. The presence of other organic solvents in the laboratory where volatile organics are analyzed can also lead to random background levels and the same precautions must be taken.

1.4 Quality Control Requirements for the VPH Method

1.4.1 General Quality Control Requirements for Determinative Chromatographic Methods

Refer to SW-846 Method 8000 for general quality control procedures for all chromatographic methods, including the VPH Method. These requirements ensure that each laboratory maintain a formal quality assurance program and records to document the quality of all chromatographic data.

Quality Control procedures necessary to evaluate the GC system operation may be found in Method 8000, Sec. 7.0, and include evaluation of calibrations and chromatographic performance of sample analyses. Instrument quality control and method performance requirements for the GC/MS system may be found in the VPH Method, Sections 10.0 and 13.0, respectively.

1.4.2 Specific QA/QC Requirements and Performance Standards for the VPH Method

Specific QA/QC requirements and performance standards for the VPH Method are presented in Table IV A-2. Strict compliance with the QA/QC requirements and performance standards for this method will provide an LSP with a presumptive certainty regarding the usability of analytical data to support MCP decisions. Widespread adherence to this approach will promote inter-laboratory consistency and provide the regulated community with a greater degree of certainty regarding the quality of data used for MCP decision-making. The issuance of these requirements and standards is in no way intended to preempt the exercise of professional judgement by the LSP in the selection of analytical methods. However, if an alternative to the recommended analytical method is chosen, the LSP is responsible to demonstrate compliance with the Response Action Performance Standard (RAPS).

1.4.3 Use of Surrogates, and LFM Samples/LFM Duplicates with Methanol-Preserved Soil/Sediment Samples

The recovery of surrogates and matrix spikes (LFM) from a soil/sediment sample that has been preserved with methanol cannot be used to directly evaluate matrix-related bias/accuracy in the conventional definition of these terms. Quality Control parameters expressed in terms of these percent recoveries (%R) may be more indicative of the variabilities associated with the analytical system (sample processing, introduction, and/or component separation and quantitation). In addition, surrogate and matrix spike recoveries may be low for samples with >25% moisture due to a dilution effect from the moisture content. This should be taken into account when

evaluating the usability of the data and the need for reanalysis. Reanalysis is generally not required if the sample contains >25% moisture (refer to Table IV A-2).

Because of this limitation, it is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze "known" concentrations and participate in relevant performance evaluation studies. Recommended practices for additional quality assurance made be found in SW-846 Methods 5000 and 8000, respectively.

This inherent limitation associated with the evaluation of matrix spike and surrogate recoveries attributable to methanol preservation of soil and sediment samples described in Appendix 4 of the VPH Method, is more than compensated for by the marked improvement in sample integrity and conservation/recoveries of the volatile analytes of concern from soil matrices.

If matrix spike (LFM) analyses are requested by the LSP for soil/sediment samples that have been preserved with methanol, the laboratory must be supplied with an adequate volume of unpreserved sample which will be used to prepare a background sample, the LFM and/or LFM Duplicate aliquots for analyses. The unpreserved soil sample submitted for percent (%) moisture may be used for this purpose. An approach to perform LFMs and/or LFM duplicates in methanol-preserved soil/sediment samples is presented in Appendix IV A-2. **It should be noted that data from the analysis of the laboratory-homogenized, methanol-preserved soil/sediment sample, designated as C_0 in Exhibit II A-1, is only representative of the background concentration in this sample and is <u>not</u> representative of the contaminant concentration at the location where the field sample was collected.**

1.4.4 Special Analytical Considerations - Addition of Surrogates and Full Matrix Spikes

Appropriate surrogates and full matrix spikes must be added to the sample through the septum seal prior to equilibration of the sample to room temperature. All samples must be shaken for 2 minutes prior to analysis. A 100 microliter (µL) aliquot of the methanol extract must then be removed and injected into 5 mL of purge water and the internal standards added to the 5 mL of purge water.

Title: Quality Assurance and Quality Control Requirements and Performance Standards for the Method For The Determination of Volatile Petroleum Hydrocarbons (VPH)

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
GC Performance	Inter-laboratory consistency and comparability	(1) n-Pentane and MTBE must be resolved from solvent front. (2) Surrogate standards must be resolved from target compounds.	No	Perform instrument/injection port maintenance as necessary.	Suspend all analyses until performance criteria are achieved. Report exceedances in the case narrative.
Retention Time Windows	Laboratory Analytical Accuracy	(1) Prior to initial calibration and when a new GC column is installed (2) Calculated according to the method. (Section 9.3) (3) Retention time windows must be updated with every CCAL.	No	NA	NA
Initial Calibration	Laboratory Analytical Accuracy	(1) Minimum of 5 standards (2) Low standard must be ≤ quantitation limit (3) %RSD should be ≤25 or "r" should be ≥0.99 for all compounds and ranges. (4) Must contain all target analytes (5) If regression analysis is used, the curve must not be forced through the origin. (6) Must meet GC performance standards.	No	Recalibrate as required by method.	Report exceedances in case narrative.
Continuing Calibration (CCAL)	Laboratory Analytical Accuracy	(1) Every 24 hours, prior to samples, and after no more than 20 samples. (2) Concentration level near midpoint of curve (3) Must contain all target analytes (4) RPD must be ≤25 for all target compounds and ranges except for naphthalene. (5) CCAL must meet GC performance standards.	No	Recalibrate as required by method. Any samples analyzed between the last CCAL that meets criteria and the one that fails criteria must be reanalyzed.	Report exceedances in case narrative.
Laboratory Method Blanks	Laboratory Method Sensitivity (contamination evaluation)	(1) Analyzed with every batch or every 20 samples, whichever is more frequent. (2) Matrix-specific (e.g., water, soil) (3) Target analytes and ranges must be < quantitation limit.	Yes	Locate source of contamination; correct problem; reanalyze associated samples.	(1) Report non-conformances in case narrative. (2)) If contamination of method blanks is suspected or present, the laboratory, using a "B" flag or some other convention, should qualify the sample results. Blank contamination should also be documented in the case narrative (3) If reanalysis is performed within holding time, the laboratory may report results of the reanalysis only. (4) If reanalysis is performed outside of holding time, the laboratory must report results of both the initial analysis and the reanalysis.

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Laboratory Control Sample (LCS); Laboratory Fortified Blank (LFB)	Laboratory Method Accuracy	(1) Analyzed with every batch or every 20 samples, whichever is more frequent. (2) Prepared using standard source different than used for initial calibration. (3) Must contain all target analytes. (4) Concentration level should be between low and mid-level standard. (5) Matrix-specific (e.g., soil, water) (6) Percent recoveries must be between 70–130 except for naphthalene. (7) Laboratories are encouraged to develop their own in-house control limits, which should fall within the limits listed above.	Yes	Recalculate the percent recoveries; Reanalyze associated samples.	(1) Report nonconformances in case narrative. (2) If re-analysis is performed within holding time, the laboratory may report results of the reanalysis only. (3) If re-analysis is performed outside of holding time, the laboratory must report results of both the initial analysis and the reanalysis.
Matrix Spike; Laboratory Fortified Matrix (LFM)	Method Accuracy in Sample Matrix	(1) Analyzed with every 20 samples (optional) (2) Matrix-specific (3) Prepared using standard source different than used for initial calibration. (4) Must contain all target compounds. (5) Concentration level should be between low and mid-level standard. (6) Percent recoveries should be between 70–130 except for naphthalene.	Yes	check LCS; if recoveries acceptable in LCS no corrective action required.	Note exceedances in case narrative.
Sample Duplicate	Method Precision in Sample Matrix	(1) Analyzed with every 20 samples (2) Matrix-specific (3) RPD should be ≤ 50.	Yes	Recheck sample calculations. Re-analyze associated samples.	Note exceedances in case narrative.
System Solvent Blank	Laboratory Method Sensitivity (contamination evaluation)	(1) Analyzed ***only*** when baseline correction is employed (2) .Analyzed with every 20 samples and after samples that are expected to be highly contaminated (3) Baseline correction may not be used if >25% of the calculated average instrument baseline	Yes (if baseline correction used)	Locate source of contamination; correct problem; reanalyze associated samples if baseline correction is >25% of the calculated average instrument baseline .	(1) Narrate all baseline corrections (2)) If System Solvent Blank correction is used, the laboratory, using a “B” flag or some other convention, should qualify the sample results. System Solvent Blank corrections should also be documented in the case narrative (3) If reanalysis is performed within holding time, the laboratory may report results of the reanalysis only. (4) If reanalysis is performed outside of holding time, the laboratory must report results of both the initial analysis and the reanalysis.

Title: Quality Assurance and Quality Control Requirements and Performance Standards for the Method For The Determination of Volatile Petroleum Hydrocarbons (VPH)

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Surrogates	Accuracy in Sample Matrix	(1) Minimum of 1 method surrogate. Recommended surrogate: 2,5-dibromotoluene. (2) Percent recoveries must be between 70-130 on both detectors. (3) Laboratories are encouraged to develop their own in-house control limits, which should fall within the limits listed above.	Yes	If one or more surrogates are outside limits, reanalyze sample unless one of the following exceptions applies: (1) obvious interference present (e.g., UCM). (2) for methanol-preserved samples, reanalysis is not required if % moisture >25 and recovery is >10%. (3) if one surrogate exhibits high recovery and target analytes are not detected in sample.	(1) Note exceedances in case narrative. (2) If reanalysis yields similar surrogate nonconformances, the laboratory should report results of both analyses. (3) If reanalysis is performed within holding time and yields acceptable surrogate recoveries, the laboratory may report results of the reanalysis only. (4) If reanalysis is performed outside of holding time and yields acceptable surrogate recoveries, the laboratory must report results of both the initial and reanalysis. (5) If sample is not reanalyzed due to obvious interference, the laboratory must provide the chromatogram in the data report.
General Reporting Issues	NA	(1) The laboratory should report values ≥ the sample-specific reporting limit. (2) Dilutions: If diluted and undiluted analyses are performed, the laboratory should report results for the lowest dilution within the valid calibration range for each analyte. The associated QC (e.g., method blanks, surrogates, etc.) for each analysis must be reported. (3) The height of UCM or single non-target compounds must be less than the height of the highest demonstrated linear standard. (4) All information required in Appendix 3 of the method must be provided for each sample in a "clear and concise manner."			(1) Reporting of diluted and undiluted analyses required.

GC = Gas Chromatography
MS = Matrix Spike
%RSD = Percent Relative Standard Deviation
NA = Not Applicable

"r" = Correlation Coefficient
RPDs = Relative Percent Differences
UCM = Unresolved Complex Mixture

1.5 Analyte List for the VPH Method

As described in Section 1.1, the VPH Method is designed to complement and support the toxicological approach developed by the Massachusetts Department of Environmental Protection to evaluate human health hazards that may result from exposure to petroleum hydrocarbons (MADEP, 1994). It is intended to produce analytical data in a format suitable for evaluation by that approach, and that may also be compared to reporting and cleanup standards promulgated in the Massachusetts Contingency Plan (310 CMR 40.0000).

The analyte list for the VPH Method is presented in Table IV A-3. The list is comprised of eight (8) Target Analytes and three (3) collectively quantified volatile hydrocarbon ranges as identified in Appendix 3 of the VPH Method. The quantification of the specified hydrocarbon ranges is a specific requirement of the VPH Method. This Method may also be used to identify and quantify the listed Target Analytes at the discretion of the LSP.

Table IV A-3 Volatile Petroleum Hydrocarbons (VPH) Method Analyte List

Range/Target Analyte	CASRN	MCP METHOD 1	
		GW-1 (GW-2)	S-1/GW-1
		µg/L (ppb)	µg/g (ppm)
Volatile Petroleum Hydrocarbon Ranges:			
C5-C8 Aliphatic Hydrocarbons	NA[1]	400	100
C9-C12 Aliphatic Hydrocarbons	NA[1]	(1000)	1000
C9-C10 Aromatic Hydrocarbons	NA[1]	200	100
Target Analytes:			
Benzene	71432	5	10
Ethylbenzene	100414	700	80
Methyl-tert-butylether	1634044	70	0.3
Naphthalene	91203	20	4
Toluene	108883	1000	90
o-Xylene[3]	95476	(6,000)	500
m- Xylene[2,3]	108383	(6,000)	500
p- Xylene[2,3]	106423	(6,000)	500

1.NA = Not Applicable

2. May not be resolvable under chromatographic conditions required under this Method

3. May be reported and evaluated as mixed isomers

2.0 DATA USABILITY ASSESSMENT FOR THE VPH METHOD

Overall data usability is influenced by uncertainties associated with both sampling and analytical activities. This document provides detailed quality assurance requirements and performance standards for the VPH Method which may be used to assess the analytical component of data usability. The sampling component of data usability, an independent assessment of the effectiveness of sampling activities to meet data quality objectives, is not substantively addressed in this document. Sample preservation, container and analytical holding time specifications for surface water, groundwater, soil, and sediment matrices for samples analyzed for VPH in support of MCP decision-making are presented in Appendix IV A–1 of this document and Appendix VII-A, WSC-CAM-VIIA, Quality Assurance and Quality Control Guidelines for Sampling, Data Evaluation and Reporting Activities.

A data usability assessment is a critical and required component for all analytical deliverables used in MCP decision-making. Generally, the data usability assessment addresses three (3) major issues:

1. How will laboratory data be reconciled with the data quality objectives?
2. How will data quality issues, if noted, be addressed?
3. How will the limitations on the use of the data be reported and managed by the decision-makers?

It should be clearly understood that the data usability assessment is the final step in the data evaluation process and can only be performed on data of known and documented quality.

Determining the usability of analytical data begins with the review of field and laboratory QC samples and qualifiers to assess analytical performance of the field collection, laboratory procedures, and the analytical method in relation to the sample matrix. The focus of this evaluation should be on how limitations may affect overall data usability rather than trying to determine the source or cause of the error (although the source or cause of error may be important in defining re-sampling and re-analysis requirements for critical data gaps). This assessment is based on a critical evaluation of the six (6) data quality indicators: precision, accuracy, representativeness, comparability, completeness, and sensitivity (a.k.a., PARCCS parameters). Specific qualitative and quantitative acceptance criteria for individual PARCCS parameters must be established by the user of the data at the onset of the program.

2.1 Specific Guidance Regarding the Interpretation and Use of VPH Data

The VPH Method produces both analyte-specific (target analytes) and method defined (hydrocarbon fractions) data. An analyte-specific approach produces data by comparing the response of a known analyte with an unknown concentration to the response of a standard for the same analyte with a known concentration under the same analytical conditions. A method-defined approach produces data by prescriptively defining both analytical conditions and assumptions used to calibrate and interpret the data produced. Such an approach is particularly useful in determining average characteristics for a limited set of analytes with similar physical, chemical and toxological properties (i.e., the collective concentration of a limited range of hydrocarbons). However, a clear understanding of the analytical limitations of the method and assumptions used to interpret data are required to maximize the potential of using this approach.

Both target analytes and hydrocarbon ranges are subject to potential "false positive" bias associated with non-specific gas chromatographic analysis. That is (1) other compounds co-eluting at the specified retention time may be falsely identified and/or quantified (false positive) as a Target Analyte; (2) compounds not meeting the regulatory definition of the aromatic and/or aliphatic fractions defined in Sections 3.4 and 3.5 of the Method, respectively, that may elute within the method-defined retention time window would be included in the Peak Area Calculation (PAC) and result in an overestimation of a fraction's concentration; or, (3) as described in Section 4.4 of the VPH Method, non-aromatic compounds that may elute between o-xylene and naphthalene and elicit a response on the PID would be included in the PAC, resulting in an overestimation of the C_9 through C_{10} aromatic fraction's concentration.

Confirmatory analysis by a Gas Chromatography/Mass Spectroscopy (GC/MS) procedure or other suitable method, is recommended in cases where a Target Analyte reported by this method exceeds an applicable reporting or cleanup standard, and/or where co-elution of a hydrocarbon compound not meeting the regulatory definition of a specific hydrocarbon fraction is suspected. Dual-column confirmation is suitable for Target Analytes only.

The following definitions are provided to assist in the interpretation and evaluation of Volatile Petroleum Hydrocarbon data:

Aliphatic Hydrocarbon: Any organic compound comprised solely of carbon and hydrogen characterized by a straight, branched or cyclic chain of carbon atoms. By definition, this class of organic compounds includes alkanes, alkenes, alkynes, cycloalkanes or cycloalkenes for the VPH methodology.

Aromatic Hydrocarbon: Any cyclic and conjugated organic compound comprised solely of carbon and hydrogen. Aromatic compounds of environmental significance are benzoids that contain benzene or fused benzene rings.

Volatile Petroleum Hydrocarbon: Any hydrocarbon that elutes within the C_5 through C_8, and C_9 through C_{12} aliphatic ranges or the C_9 through C_{10} aromatic ranges defined by the method. The definition of Volatile Petroleum Hydrocarbon specifically **excludes** all substituted aliphatic or aromatic hydrocarbon derivatives (non-hydrocarbons as defined by the VPH Method), the individual VPH Method Target Analytes, surrogates, and/or internal standards that co-elute within these method-specific ranges. The VPH Method is suitable for the separation and quantification of the aliphatic and non-target aromatic components of gasoline, mineral spirits, certain petroleum naphthas and components of kerosene, jet fuel, heating oils, lubricating oils, and/or other petroleum products contained within the aforementioned method-defined ranges.

2.1.1 Interfering Peaks in Specified Aliphatic Hydrocarbon Ranges

Hydrocarbons (and non-hydrocarbons), even with elution times within the defined chromatographic windows for the aliphatic hydrocarbon ranges specified by the VPH Method, need not be included in the PAC for these ranges unless they meet the definitions of aliphatic hydrocarbon and volatile petroleum hydrocarbon, as defined above. If the concentration of a hydrocarbon range is based on one (or just a few) peaks within the range and an indicative petroleum hydrocarbon peak pattern is not apparent , the laboratory should provide this information and alert the data user of the potential for a false positive result in the case narrative. MCP sites with chlorinated hydrocarbons, ketones, and/or co-mingled non-petroleum hydrocarbons are subject to this interference.

2.1.2 Interfering Peaks in Specified Aromatic Hydrocarbon Range

The VPH Method should be used with caution at sites with an uncertain history, particularly closed or abandoned Manufactured Gas Plants (MGPs). Styrene, a common contaminant of concern (COC) at many MGP sites, can not be satisfactorily resolved from o-xylene under the chromatographic conditions specified for the VPH Method. If encountered, co-eluting styrene could cause an overestimation of o-xylene and a subsequent underestimation of the C_9-C_{10} aromatic range when the overestimated o-xylene peak is subtracted from the PAC for the range. Other contaminant pairs routinely encountered at MCP sites that are difficult to resolve under the chromatographic conditions specified for the VPH Method, include 1,2-dichloroethane/benzene and 1,1,1,2-tetrachloroethane/ethylbenzene.

2.1.3 Evaluation of Interfering Compounds Not Associated with a Petroleum Product

In general, it may be prudent to confirm all PID/FID data by SW-846 Method 8260B (GC/MS) if critical MCP decision making (notification, compliance with cleanup standards, risk assessment, etc.) is based solely on the VPH Method (or any other non-specific GC analysis). If a positive interference is suspected from hydrocarbons and/or non-hydrocarbons not associated with VPH in either an aliphatic or aromatic fraction or with a Target Analyte, and such interference would adversely effect MCP decision making, if confirmed, then SW-846 Method 8260B, Volatile Organics by GC/MS should be employed to accurately identify and quantify of the components that comprise the fraction or to resolve the analyte pairs.

It is recommended that the chromatographic conditions specified under SW-846 Method 8260B be modified for consistency with the conditions specified by the VPH Method to better allow for a direct comparison of the suspect PID/FID peaks with the GC/MS system. This is particularly useful when comparing suspect aliphatic hydrocarbons. The electron impact mass spectra for aliphatic hydrocarbon homologues are not particularly unique and chromatographic relative retention time data may also be required to confirm VPH data.

2.1.4 PID Response to Non-Aromatic Compounds

Although not a predominant component in petroleum hydrocarbon mixtures, alkenes and other non-aromatic hydrocarbons can elicit a positive PID response. In general, the PID response to these non-aromatic compounds is weaker than the response for the same mass of an aromatic hydrocarbon. However, at elevated concentrations, these non–aromatic compounds may interfere or yield false positives (high positive bias) to aromatic target analytes or range concentrations. This condition can be somewhat mitigated by using a lower energy lamp in the PID assembly of the gas chromatograph. Such a change would result in a loss of sensitivity and is considered a major instrument modification that would require recalibration and a re-demonstration of performance.

2.2 Substitution of GC/MS for the Identification and Quantification of VPH Ranges and Target Analytes

Consistent with Section 11.3.2.1 of the VPH Method, substitution of GC/MS for conventional GC detection for the identification and quantification of VPH ranges and/or target analytes is considered a significant modification. Modifications to the VPH Method are permissible, provided that adequate documentation exists or has been developed, to demonstrate an equivalent or superior level of performance. All significant modifications must be disclosed and described on the data report form, as detailed in Section 11.3 of the VPH Method.

3.0 Reporting Requirements for the VPH Method

General reporting requirements for analytical data used in support of assessment and evaluation decisions at MCP disposal sites are presented in WSC-CAM-VIIA, "Quality Assurance and Quality Control Guidelines for Sampling, Data Evaluation, and Reporting Activities for the Massachusetts Contingency Plan (MCP)". This guidance document provides recommendations for field QA/QC, the required content of the Environmental Laboratory Report and case narrative, and the LSP's Data Assessment Report.

Specific QA/QC Requirements and Performance Standards for the VPH Method are presented in Table IV A-2. Specific reporting requirements for the VPH Method are summarized below in Table IV A-4 as "Required Analytical Deliverables (**YES**)". These routine reporting requirements should always be included as part of the laboratory deliverable for this method. It should be noted that although certain items are not specified as "Required Analytical Deliverables (**NO**)", these data are to be available for review during an audit and may also be requested on a client-specific basis.

Table IV A-4 Analytical Reporting Requirements for VPH Method

Parameter	Method Section Reference	Required Analytical Deliverable
GC Performance	10.2.1	NO
Retention Time Windows	10.2.2	NO
Initial Calibration	10.2.3	NO
Calibration Check Standard [1]	10.4.2.1	NO
Laboratory Method Blank[1]	10.4.2.2	YES
Laboratory Fortified Blank (LFB)[1]	10.4.2.3	YES
Laboratory Fortified Matrix (LFM) [1]	10.4.3.1	Discretionary
Laboratory Fortified Matrix Duplicate (LFMD) [1]	10.4.3.1	Discretionary
Sample Duplicate	10.2.2.4	YES
Surrogates	10.4.1	YES
System Solvent Blank	10.4.2.5	Required for baseline correction per 11.2.4
Trip Blank (aqueous or methanol)	10.1.2	Must accompany each sample batch
Internal Standards (ISs)	9.4.2	NO
General Reporting Issues	11.3	Required data reporting format is presented in Section 11.3

[1] VPH Method - specific terminology

Appendix IV-A I

Sample Collection, Preservation, And Handling Procedures for the VPH Method

1.0 Sampling

Sample preservation, container and analytical holding time specifications for surface water, groundwater, soil, and sediment matrices for VPH samples analyzed in support of MCP decision-making are summarized below and presented in Appendix VII-A of WSC-CAM-VIIA, Quality Assurance and Quality Control Guidelines for Sampling, Data Evaluation, and Reporting Activities for the Massachusetts Contingency Plan (MCP).

Matrix	Container	Preservation	Holding Time
Aqueous Samples	40-mL VOC vials w/ Teflon-lined septa screw caps	Add 3 to 4 drops of 1:1 HCl either on-site or within 2 hours of collection in laboratory; **Cool to 4°C**	14 days
Soil/Sediments Samples	VOC vials w/ Teflon-lined septa screw caps. 60-mL vials: add 25 g soil 40-mL vials: add 15 g soil	1 mL methanol for every g soil; add before or at time of sampling;. Sample must be covered with methanol. **Cool to 4°C**	28 days
**** Holding time begins from time of sample collection.***			

2.0 Additional Sampling Considerations

2.1 Aqueous Samples

If effervescence occurs upon addition of HCl, samples should be collected without the acid preservative. In these instances, the analysis holding time is seven (7) days from date collected to date analyzed.

2.2 Solid Samples

Samples may be collected in a hermetically sealed sampling device, such as an EnCore™ sampler. The laboratory must transfer the contents of the EnCore™ sampler to a pre-weighed vial and preserve the sample in methanol within 48 hours of sample collection. The sample must be analyzed within 14 days of sample collection. The EnCore™ samplers must be kept at 4ºC from time of collection to time of preservation. The preserved samples must be kept at 4ºC from time of preservation until the time of analysis. Alternatively, EnCore™ samplers may also be transferred to pre-weighed vials without preservative and frozen at -10ºC ± 3ºC within 48 hours of sample collection. If frozen, the samples must be analyzed within 14 days of sample collection.

Appendix II A-2

Guidance for Performing Matrix Spike (MS) and Matrix Spike Duplicate Analyses (MSD) for Methanol-Preserved Soil/Sediment Samples Under the MCP

The following approach (spiking sample prior to methanol preservation) is recommended for laboratories requested to perform MS (LFB) and/or MSDs (LFB Duplicates) on methanol-preserved soil/sediment samples. Other analytical approaches may be used with appropriate documentation. The weights and volumes presented below should be considered nominal values. Other volumes and weights may be used as long as the 1:1 ratio of soil to methanol is maintained. Exhibit IV A-1 presents a graphic representation of this analytical approach.

1. An unpreserved aliquot of soil/sediment sample must be thoroughly homogenized in the laboratory. Some volatile compounds may be lost during processing.

2. Place a 5-gram aliquot of homogenized soil in each of three (3) pre-tared 40-ml VOA vials.

3. Cap each vial ensuring that soil particles are not entrained on the vial threads.

4. Without exposing the sample aliquot to the atmosphere, prepare an unspiked sample, designated $\mathbf{C_0}$, by adding five (5) ml of purge and trap grade methanol (previously analyzed as a system solvent blank) through the septum of the vial. Tap and agitate the sample vial.

   Note: The results of the analysis of Sample $\mathbf{C_0}$ are only representative of the concentration of the laboratory-homogenized sample (under the conditions prepared) and any contribution of the methanol preservative (determined by analysis of system solvent blank) and are not representative of the contaminant concentration at the location where the field sample was collected.

5. Without exposing the sample aliquot to the atmosphere, prepare two (2) separate spiked samples, designated $\mathbf{C_{x1}}$ and $\mathbf{C_{x2}}$, by adding 0.5 ml of the MS standard in methanol (or other appropriate solvent) to each of the remaining pre-tared VOA vials. To the extent practical, distribute the spiking solution to maximize contact with the soil matrix. Agitate the sample vials. The concentration of the MS standard will be dependent on the native concentration of the sample. Consult with the laboratory to assist in the selection of the MS standard concentration.

6. Allow vials $\mathbf{C_{x1}}$ and $\mathbf{C_{x2}}$ to equilibrate for at least 30 minutes. After the equilibration period, bring the final solvent volume in vials $\mathbf{C_{x1}}$ and $\mathbf{C_{x2}}$ up to 5ml by adding purge and trap grade methanol through the septum of each vial.

7. Proceed with analysis as described in SW-846 Method 5035/8260B for high-level VOCs using methanol preservation. **Vials may not be opened until soils are completely immersed in methanol.**

It should be noted that this procedure might result in the loss of VOCs from the native sample during the homogenization step. However, the intent of this procedure is solely to determine matrix effects and not to measure the actual concentrations present in the native sample.

Exhibit IV A –1 An Approach for Performing MS/MSDs for Methanol-Preserved Soil/Sediment Samples